

PATENT ABSTRACTS OF JAPAN

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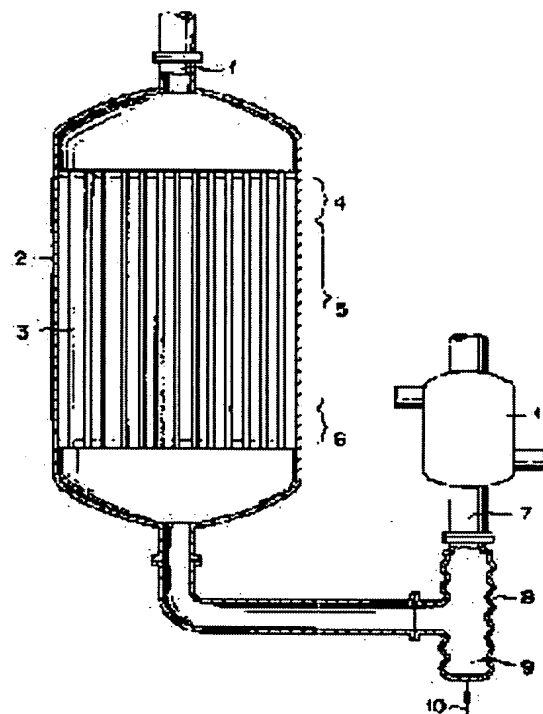
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SAWADA MASAYUKI
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(54) PRODUCTION OF ETHYLENE OXIDE

(57)Abstract:

PURPOSE: To provide a method for producing ethylene oxide, capable of preventing abnormal combustion reaction in a gas-staying part of a high- temperature part which exists on the downstream side of a reacting pipe outlet of a reactor in producing ethylene oxide by subjecting ethylene to catalytic vapor phase oxidation with a molecular oxygen.

CONSTITUTION: The characteristic of this method for producing ethylene oxide comprises feeding an inert gas from an inert gas feed pipe 10 to a gas-staying part 9 which exists on the downstream of reacting pipe outlet of a reactor used when ethylene oxide is produced by subjecting ethylene to contact vapor phase oxidation with a molecular oxygen-containing gas and in a flow zone of a gas produced by the reaction between the reaction pipe outlet and a cooling device 11. This method is safe for producing ethylene oxide by subjecting ethylene to contact vapor phase oxidation with the molecular oxygen.



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3403476

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28.02.2003

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the ethylene oxide characterized by supplying inert gas to the gas stagnation section which is a lower stream of a river, and exists in the reaction generation gas stream band of a before [a condensator] from the coil outlet of the reactor used in case contact vapor phase oxidation of the ethylene is carried out by molecular oxygen content gas and ethylene oxide is manufactured.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

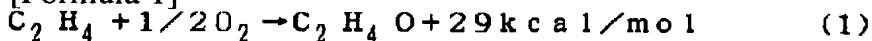
[0001]

[Industrial Application] This invention relates to the manufacture approach of ethylene oxide. When it states in detail, it faces carrying out contact vapor phase oxidation of the ethylene by molecular oxygen content gas, and manufacturing ethylene oxide, and is related with the manufacture approach of safe ethylene oxide of preventing the anomalous reaction which becomes the gas stagnation section which exists in a reaction generation gas stream band from mixing inert gas.

[0002]

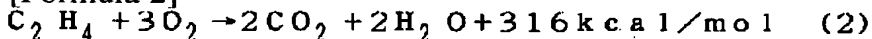
[Description of the Prior Art] In the process which carries out contact vapor phase oxidation of the contact vapor-phase-oxidation reaction of ethylene, for example, the ethylene, by molecular oxygen to the bottom of existence of a silver catalyst, and manufactures ethylene oxide Besides ethylene, saturated hydrocarbon, such as methane and ethane, nitrogen, a carbon dioxide, After the molecular oxygen content gas which consists of the hydrocarbon content gas containing an argon, oxygen, etc., air, air that carried out enrichment of the oxygen, or pure oxygen is mixed by the predetermined ratio, contact gaseous phase reaction introduced into the reactor filled up with the silver catalyst is performed. It is [0003] when ethylene is made to react to the bottom of existence of a silver catalyst by molecular oxygen in that case.

[Formula 1]



[0004]

[Formula 2]



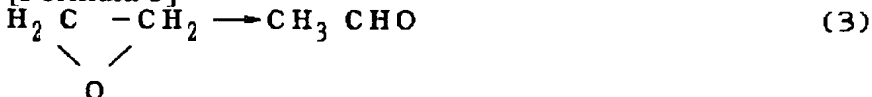
[0005] It comes out and the exothermic reaction shown is caused.

[0006] Among such exothermic reaction, in order to aim at improvement in the yield of ethylene oxide, the rate that the reaction shown by the reaction formula (1) progresses should be enlarged, and the silver catalyst, the reaction approach, etc. are examined. However, it is unavoidable that the complete oxidation reaction of ethylene large, a reaction formula (2), i.e., heat of reaction, now occurs in coincidence.

[0007] Moreover, there is a reaction which affects the yield of ethylene oxide in addition to said reaction formula (1) and a reaction formula (2). It is the isomerization to the acetaldehyde which advances by the reaction formula shown by the next reaction formula (3) of the generated ethylene oxide.

[0008]

[Formula 3]

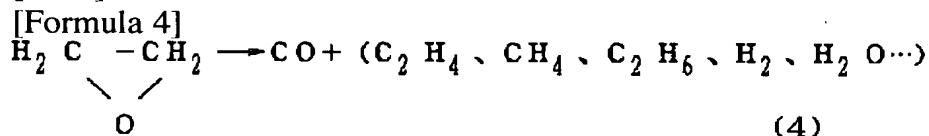


[0009] Therefore, however high the selectivity to the ethylene oxide of ethylene may be, if there is much

isomerization to the acetaldehyde of the generated ethylene oxide, the yield fall of ethylene oxide will be caused.

[0010] Moreover, the anomalous reaction to the carbon monoxide which runs by the reaction formula shown by the following reaction formula (4), hydrocarbons (methane, ethane, ethylene, etc.), hydrogen, and water occurs. It is one of the big technical problems in ethylene oxide manufacture to lose an anomalous reaction from the coil outlet of a reactor, since a down-stream reaction generation gas stream band is high temperature.

[0011]



[0012] From the need of ethylene oxide growing in recent years, in order to aim at reduction of the manufacturing cost of ethylene oxide, enlargement of an ethylene oxide manufacturing plant is advanced. Therefore, in carrying out contact vapor phase oxidation of the ethylene by molecular oxygen, and manufacturing ethylene oxide, how an ethylene oxide manufacturing plant is operated safely has a big problem on insurance and economy.

[0013] The method of generally letting reaction generation gas pass in the cooling region filled up with packing in the contact vapor-phase-oxidation method by the molecular oxygen of a hydrocarbon for an anomalous reaction and side reaction control is well-known (JP,39-17254,B). Moreover, it is also well-known to apply to the approach of manufacturing ethylene oxide by the contact vapor-phase-oxidation method according such an approach to the molecular oxygen of ethylene. for example, according to JP,51-4101,A, the reaction zone was adjoined -- it is -- it is -- the inactive ingredient was contained without adjoining -- it is -- it is -- the resultant acquired [in the cooling region which is not contained] in a reaction zone is passed. Moreover, according to JP,53-2409,A, the cooling region filled up with the inactive fireproof granular object which has the surface area below 0.1m² / g for a resultant is passed.

[0014]

[Problem(s) to be Solved by the Invention] The multipipe heat exchange mold reactor of the reactor with which it is used at the time of carrying out contact vapor phase oxidation to ethylene by molecular oxygen, and manufacturing ethylene oxide conventionally has an expansion joint for the destructive prevention by the thermal stress of the manhole for safety and workability (a drawing given in JP,54-32408,A, drawing given in JP,63-190881,A), the relief valve of abnormality pressure-buildup prevention and a rupture disk, a manometer, a thermometer, and the piping section etc., and the gas stagnation section exists. However, there was a problem that an abnormality combustion reaction occurred in these gas stagnation sections.

[0015] This invention is to offer the manufacture approach of the ethylene oxide which protects an abnormality combustion reaction from the coil outlet of the reactor at the time of carrying out contact vapor phase oxidation by above mentioned ethylene and molecular oxygen, and manufacturing ethylene oxide in the gas stagnation section which exists in a 200-300-degree C down-stream reaction generation gas stream band.

[0016]

[Means for Solving the Problem] This invention relates to the manufacture approach of the ethylene oxide characterized by supplying inert gas to the gas stagnation section which is a lower stream of a river, and exists in the reaction generation gas stream band between condensators from the coil outlet of the reactor used in case contact vapor phase oxidation of the ethylene is carried out by molecular oxygen content gas and ethylene oxide is manufactured.

[0017] In this invention, the gas stagnation section of the gas outlet section of a reactor has an expansion joint for the destructive prevention by the thermal stress of the manhole for paths installed in the coil outlet of the reactor with which it is used at the time of carrying out contact vapor phase oxidation to ethylene by molecular oxygen, and manufacturing ethylene oxide, for example, a multipipe heat

exchange mold reactor, a relief valve, a rupture disk, a manometer, a thermometer, and the piping section etc. 200-300 degrees C of temperature of such the gas stagnation section are 210-280 degrees C preferably.

[0018] As inert gas used by this invention, nitrogen, carbon dioxide gas, methane, an argon, etc. are mentioned, and it is nitrogen preferably. Preferably, the retention time defined as the stagnation section of said reaction generation gas by the following formula can supply the amount of supply of inert gas for 1 to 10 hours for less than 12 hours, as it has been 3 - 8 hours still more preferably.

[0019]

[Equation 1]

ガス滞留時間 (min)

= 滞留部容積 (m³) / 実際の温度圧力下での不活性ガス流量 (m³ / min)

[0020] As an inert packing material with which the preheating section and the inactive substance restoration section of a reactor of this invention are filled up, although all can be used regardless of a ball, a semi-sphere, a pellet, a ring, and amorphism, the alumina usually used as desirable support for silver catalysts, silica alumina, a zirconia, a magnesia, silicon carbide, etc. are desirable, and stainless steel, alpha-alumina, and a zirconia are [that what is necessary is just an inactive refractoriness object] especially desirable. The configuration of such inactive refractoriness support, a dimension, a hole, specific surface area, apparent porosity, etc. can be suitably chosen in consideration of the pressure loss at the time of filling up a coil, and a mechanical strength. 16 - 1/2 inch per /, mean diameters are 3 / 16 - 1/2 inch, and a ball thru/or its ring-like object are usually preferably desirable. Moreover, what deposited at least one sort chosen as the above-mentioned inactive refractoriness support from sodium, a potassium, a rubidium, caesium, a lithium, calcium, strontium, barium, and a thallium can use it suitably, and sodium, a potassium, a rubidium, caesium, and a thallium are especially desirable. As for especially these, it is desirable to fill up the coil of the inactive substance restoration section.

[0021] The process and reaction condition which can apply this invention approach can apply both a well-known process and a reaction condition in this field conventionally. For example, the process which carries out contact vapor phase oxidation of the ethylene by molecular oxygen, and manufactures ethylene oxide can apply this invention approach effectively [in any case], although there are an air-oxidation method for using air as a source of oxygen and an oxygen acid-ized method using pure oxygen. The oxygen acid-ized method which can enlarge reacting weight per one catalyst bed passage, and can make ethylene oxide concentration high especially can apply effectively.

[0022] Although material gas mixture consists of reaction inhibitors, such as ethylene, oxygen, carbon dioxide gas, nitrogen, an argon, methane, ethane, and 2 chlorination ethane, etc. in the operating condition, and ethylene concentration is so advantageous that it is high, it is 15 to 35 capacity % especially below 40 capacity %. Especially carbon dioxide gas is four to 8 capacity % below 10 capacity %. Moreover, since methane has the operation which shifts range of explosion to an insurance side, and narrows range of explosion when methane or ethane is made to exist in gas, it is effective to exist by high concentration considerably as a reactant gas diluent.

[0023] Reaction pressure is 1.08-3.04MPa preferably 0.59 to 4.02 MPa. 150-300 degrees C of reaction temperature are 180-280 degrees C preferably. space velocity -- 1000-10000hr⁻¹ -- it is 2000-8000hr⁻¹ preferably.

[0024] Although all of a well-known silver catalyst can be conventionally used for the catalyst with which the reaction section is filled up Preferably below specific surface area of 20m² / g 0.01-10m² / g, What carried out deposit support of the metal silver of a minute amount is preferably good for the inactive refractoriness support of 30 - 70 capacity % more than apparent porosity 20 capacity %. Moreover, what added at least one sort chosen from at least a kind of alkali metal and the alkaline earth metal which are chosen from caesium, a potassium, and a rubidium as a reaction accelerator, a thallium, antimony, tin, etc. is desirable. The inactive refractoriness support which can use inactive refractoriness support, such as an alumina, a silica alumina, silicon carbide, a zirconia, and a magnesia, as a support ingredient, and uses especially alpha-alumina as a principal component is desirable. Although the

configuration of support-has a ball, a semi-sphere, a ring, a pellet, etc., a ball thru/or its ring are desirable. Moreover, the mean diameter has desirable 1 / 16 - 1/2 inch, and especially its 3 / 16 - 5/16 inch are desirable. The amount of the silver supported is good at 1 - 20 % of the weight in a catalyst, and 5 - 15% of the weight of its range is substantially economical especially.

[0025] In order to explain this invention in more detail, a drawing explains. A drawing does not show 1 of the embodiment at the time of carrying out contact vapor phase oxidation of the ethylene by molecular oxygen content gas, and the equipment used under existence of a silver catalyst, and does not restrain this invention.

[0026] In drawing 1, it consists of many coils. To the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 which formed the preheating section 4 which filled up the inlet-port section of a coil with the inactive substance, and with which it was filled up, the reaction section 5 filled up with the silver catalyst between the inlet-port section of a coil, and the outlet section, or the inert-packing-material restoration section 6 which filled up the outlet section of a coil with the inert packing material, and ethylene, oxygen, The temperature containing reaction inhibitors, such as carbon dioxide gas, nitrogen and an argon, methane, ethane, and 2 chlorination ethane, etc. of 100-200 degrees C, It is introduced from a conduit 1. desirable -- 150-190-degree C material gas -- material gas supply -- pass the preheating section 4, the reaction section 5, and the inert-packing-material restoration section 6 -- reaction generation gas -- 200-300 degrees C is preferably sent to the condensator 11 for cooling of 210-280-degree C reaction generation gas through a conduit 7.

[0027] This invention consists of many coils 3. And between the preheating section 4 and the inlet-port section of a coil which filled up the inlet-port section of a coil with the inactive substance and with which it was filled up, and the outlet section A silver catalyst In the reaction section 5 with which it was filled up, or the outlet section of a coil, an inert packing material The inert-packing-material restoration section 6 with which it was filled up The established silver catalyst of the vertical mold multipipe heat exchange mold reactor 2 At the place left without adjoining the reaction section 5 with which it was filled up reaction generation gas It is effective in the process which installed the condensator for cooling reaction generation gas in the place left without adjoining the inert-packing-material restoration section 6 filled up with the process which installed the condensator 11 for cooling, or the silver catalyst of the vertical mold multipipe heat exchange mold reactor 2. A condensator 11 has a condensator with a heat exchanger, water, air, etc. for carrying out heat exchange of the material gas and reaction generation gas which are supplied to the boiler for heat recovery, and a reactor etc.

[0028] Supply of the inert gas of this invention can supply inert gas to the stagnation section of reaction generation gas, such as an expansion joint for the destructive prevention by the thermal stress of the manhole of the working-level month installed in the 200-300-degree C reaction generation gas stream band between the down-stream heat exchangers 11 from the coil outlet of the vertical mold multipipe heat exchange mold reactor 2, a relief valve, a rupture disk, a manometer, a thermometer, and the piping section. drawing 1 -- setting -- the gas stagnation section 9 of an expansion joint 8 -- inert gas supply -- inert gas is supplied from a conduit.

[0029] The gas stagnation section which exists in the reaction generation gas stream band of 200-300 degrees C of lower streams of rivers from the coil outlet of the reactor of this invention can be filled up with the inactive substance of a network, Paul ring, Raschig ring, and a saddle configuration.

[0030] drawing 2 shows other embodiments of this invention, and the gas stagnation section 12 forms it in the manhole 14 of the lower part of a reactor 2 -- having -- inert gas supply -- inert gas is supplied to the gas stagnation section from a conduit 13. In addition, in this drawing, the same sign as drawing 1 expresses the same member.

[0031]
[Function] the lower part [section / of the reactor at the time of carry out contact vapor phase oxidation of this invention by said ethylene and molecular oxygen which be carried out , and manufacture ethylene oxide / coil outlet] -- and while cancel generating of an abnormalities combustion reaction in the gas stagnation section which exist in exist in the reaction generation gas stream band of a before [a heat exchanger] , the stability of thermal efficiency aim at and the operation which can increase the

effectiveness which control the isomerization to the acetaldehyde which be an impurity offer .

[0032]

[Example] Hereafter, an example explains this invention in more detail. However, this example is one mode of invention and does not regulate this invention.

[0033] In example 1 drawing 1 Ethylene 20 capacity %, Through a conduit 1, space-velocity 5000hr-1 appears in the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 comparatively, and it introduces. the material gas of 2.36MPa(s) by which the preheating was carried out to the temperature containing molecular oxygen 8 capacity % and carbon-dioxide 6 capacity % of 180 degrees C -- material gas supply -- pass the preheating section 4 filled up with the inactive substance, the reaction section 5 filled up with the silver catalyst, and the inactive substance restoration section 6 -- the 242-degree C reaction generation gas containing generation ethylene oxide 2 capacity % -- reaction generation gas -- it sent to the condenser 11 through the conduit 7.

[0034] on the other hand -- the reaction generation gas of the coil outlet of the multipipe heat exchange mold reactor 2 -- a conduit 7 and reaction generation gas -- the gas stagnation section 9 (phi650mmx660mm and 0.22m3) (temperature of 242 degrees C) of the expansion-joint section 8 for piping thermal stress prevention installed between conduits 10 -- inert gas supply -- nitrogen gas was supplied through the conduit 10. the reaction generation gas of the downstream of after 1000-hour operation and the expansion joint 8 for piping thermal stress prevention -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 0.05 capacity ppm and the aldehyde 2 capacity ppm. Moreover, as a result of carrying out the release check of the gas stagnation section 7, there was no adhesion generation of carbide. A result is shown in Table 1.

[0035] example of comparison 1 example 1 -- setting -- the gas stagnation section 9 of the expansion-joint section 8 for piping thermal stress prevention -- inert gas supply -- it carried out like the example 1 except not supplying nitrogen gas through a conduit 10. After 13-hour operation, since the temperature of suddenly reaction generation gas rose to 316 degrees C, urgent shutdown was carried out. the reaction generation gas of the downstream of the expansion joint 8 for piping thermal stress prevention -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 5000 capacity ppm and the aldehyde 1000 capacity ppm (as an acetaldehyde). Moreover, as a result of carrying out the release check of the gas stagnation section 9, adhesion generation of carbide was seen. A result is shown in Table 1.

[0036]

[Table 1]

| | | 実施例 1 | 比較例 1 |
|---------------------------|-------|--------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.22 | 0.22 |
| ガス滞留時間 (min.) | 滞留部 9 | 404 | 780 |
| 窒素ガス投入量 (NI/min) | 導管 10 | 7 | 0 |
| 反応生成ガス温度 (°C) | 導管 7 | 242 | 242→316 |
| CO濃度 (ppm) | 導管 7 | 0.05以下 | 1→5000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→1000 |

[0037] In example 2 drawing 2 Ethylene 20 capacity %, Through a conduit 1, space-velocity 5000hr-1 appears in the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 comparatively, and it introduces. the material gas of 2.36MPa(s) by which the preheating was carried out to the temperature containing molecular oxygen 8 capacity % and carbon-dioxide 6 capacity % of 180 degrees C -- material gas supply -- pass the preheating section 4 filled up with the inactive substance, and the reaction section

5 filled up with the silver catalyst -- the 244-degree C reaction generation gas containing generation ethylene oxide 2 capacity % -- reaction generation gas -- it sent to the condensator (not shown) through the conduit 7.

[0038] on the other hand -- the coil outlet of the multipipe heat exchange mold reactor 2, and reaction generation gas -- the gas stagnation section 12 (phi600mmx600mm and 0.17m³) of the manhole 14 installed between conduits 7 -- inert gas supply -- carbon dioxide gas was supplied through the conduit 13. the reaction generation gas of the downstream of after 1200-hour operation and a manhole 8 -- as a result of a conduit's 7 analyzing, it was the aldehyde 2 capacity ppm below the carbon monoxide 0.05 capacity ppm. Moreover, as a result of carrying out the release check of the gas stagnation section 12, there was no adhesion generation of carbide. A result is shown in Table 2.

[0039] example of comparison 2 example 2 -- setting -- the gas stagnation section 12 of a manhole 14 -- inert gas supply -- it carried out like the example 2 except not supplying carbon dioxide gas through a conduit 13. After 20-hour operation, since the temperature of suddenly reaction generation gas rose to 314 degrees C, urgent shutdown was carried out. the reaction generation gas of the downstream of the gas stagnation section 12 of a manhole 14 -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 6000 capacity ppm and the aldehyde 1300 capacity ppm (as an acetaldehyde). Moreover, as a result of carrying out the release check of the gas stagnation section 9, adhesion generation of carbide was seen. A result is shown in Table 2.

[0040]

[Table 2]

| | | 実施例 2 | 比較例 2 |
|---------------------------|-------|--------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.17 | 0.17 |
| ガス滞留時間 (min) | 滞留部 9 | 437 | 1200 |
| 炭酸ガス投入量 (NI/min) | 導管 10 | 5 | 0 |
| 反応生成ガス温度 (°C) | 導管 7 | 244 | 244→314 |
| CO濃度 (ppm) | 導管 7 | 0.05以下 | 1→6000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→1300 |

[0041]

[Effect of the Invention] the 200-300-degree C elevated temperature section which exist in the coil outlet section of the reactor at the time of carry out contact vapor phase oxidation of this invention by said ethylene and molecular oxygen carried out, and manufacture ethylene oxide -- a lower stream of a river -- and while cancel generating of an abnormalities combustion reaction in the gas stagnation section which exist in the reaction generation gas stream band of a before [a condensator], the stability of thermal efficiency aim at and it have the effectiveness that the effectiveness which control the isomerization to the acetaldehyde which be an impurity can increase.

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TECHNICAL FIELD

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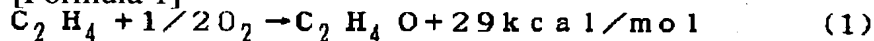
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PRIOR ART

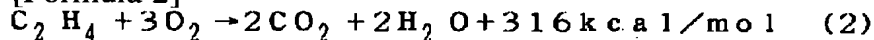
[Description of the Prior Art] In the process which carries out contact vapor phase oxidation of the contact vapor-phase-oxidation reaction of ethylene, for example, the ethylene, by molecular oxygen to the bottom of existence of a silver catalyst, and manufactures ethylene oxide Besides ethylene, saturated hydrocarbon, such as methane and ethane, nitrogen, a carbon dioxide, After the molecular oxygen content gas which consists of the hydrocarbon content gas containing an argon, oxygen, etc., air, air that carried out enrichment of the oxygen, or pure oxygen is mixed by the predetermined ratio, contact gaseous phase reaction introduced into the reactor filled up with the silver catalyst is performed. It is [0003] when ethylene is made to react to the bottom of existence of a silver catalyst by molecular oxygen in that case.

[Formula 1]



[0004]

[Formula 2]



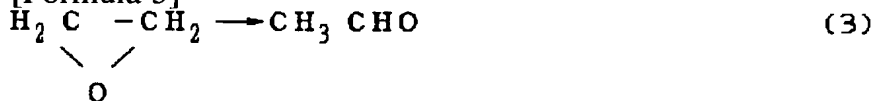
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[0007] Moreover, there is a reaction which affects the yield of ethylene oxide in addition to said reaction formula (1) and a reaction formula (2). It is the isomerization to the acetaldehyde which advances by the reaction formula shown by the next reaction formula (3) of the generated ethylene oxide.

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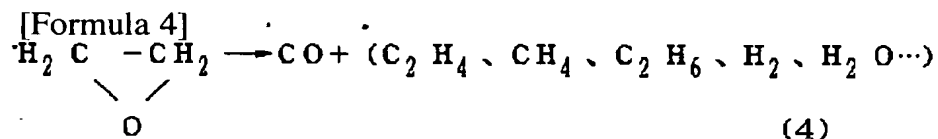
[Formula 3]



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[0010] Moreover, the anomalous reaction to the carbon monoxide which runs by the reaction formula shown by the following reaction formula (4), hydrocarbons (methane, ethane, ethylene, etc.), hydrogen, and water occurs. It is one of the big technical problems in ethylene oxide manufacture to lose an anomalous reaction from the coil outlet of a reactor, since a down-stream reaction generation gas stream band is high temperature.

[0011]



[0012] From the need of ethylene oxide growing in recent years, in order to aim at reduction of the manufacturing cost of ethylene oxide, enlargement of an ethylene oxide manufacturing plant is advanced. Therefore, in carrying out contact vapor phase oxidation of the ethylene by molecular oxygen, and manufacturing ethylene oxide, how an ethylene oxide manufacturing plant is operated safely has a big problem on insurance and economy.

[0013] The method of generally letting reaction generation gas pass in the cooling region filled up with packing in the contact vapor-phase-oxidation method by the molecular oxygen of a hydrocarbon for an anomalous reaction and side reaction control is well-known (JP,39-17254,B). Moreover, it is also well-known to apply to the approach of manufacturing ethylene oxide by the contact vapor-phase-oxidation method according such an approach to the molecular oxygen of ethylene. for example, according to JP,51-4101,A, the reaction zone was adjoined -- it is -- it is -- the inactive ingredient was contained without adjoining -- it is -- it is -- the resultant acquired [in the cooling region which is not contained] in a reaction zone is passed. Moreover, according to JP,53-2409,A, the cooling region filled up with the inactive fireproof granular object which has the surface area below 0.1m² / g for a resultant is passed.

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EFFECT OF THE INVENTION

[Effect of the Invention] the 200-300-degree C elevated temperature section which exist in the coil outlet section of the reactor at the time of carry out contact vapor phase oxidation of this invention by said ethylene and molecular oxygen carried out , and manufacture ethylene oxide -- a lower stream of a river -- and while cancel generating of an abnormalities combustion reaction in the gas stagnation section which exist in the reaction generation gas stream band of a before [a condensator] , the stability of thermal efficiency aim at and it have the effectiveness that the effectiveness which control the isomerization to the acetaldehyde which be an impurity can increase .

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TECHNICAL PROBLEM

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[0015] This invention is to offer the manufacture approach of the ethylene oxide which protects an abnormality combustion reaction from the coil outlet of the reactor at the time of carrying out contact vapor phase oxidation by above mentioned ethylene and molecular oxygen, and manufacturing ethylene oxide in the gas stagnation section which exists in a 200-300-degree C down-stream reaction generation gas stream band.

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MEANS

[Means for Solving the Problem] This invention relates to the manufacture approach of the ethylene oxide characterized by supplying inert gas to the gas stagnation section which is a lower stream of a river, and exists in the reaction generation gas stream band between condensators from the coil outlet of the reactor used in case contact vapor phase oxidation of the ethylene is carried out by molecular oxygen content gas and ethylene oxide is manufactured.

[0017] In this invention, the gas stagnation section of the gas outlet section of a reactor has an expansion joint for the destructive prevention by the thermal stress of the manhole for paths installed in the coil outlet of the reactor with which it is used at the time of carrying out contact vapor phase oxidation to ethylene by molecular oxygen, and manufacturing ethylene oxide, for example, a multipipe heat exchange mold reactor, a relief valve, a rupture disk, a manometer, a thermometer, and the piping section etc. 200-300 degrees C of temperature of such the gas stagnation section are 210-280 degrees C preferably.

[0018] As inert gas used by this invention, nitrogen, carbon dioxide gas, methane, an argon, etc. are mentioned, and it is nitrogen preferably. Preferably, the retention time defined as the stagnation section of said reaction generation gas by the following formula can supply the amount of supply of inert gas for 1 to 10 hours for less than 12 hours, as it has been 3 - 8 hours still more preferably.

[0019]

[Equation 1]

ガス滞留時間 (min)

= 滞留部容積 (m³) / 実際の温度圧力下での不活性ガス流量 (m³ / min)

[0020] As an inert packing material with which the preheating section and the inactive substance restoration section of a reactor of this invention are filled up, although all can be used regardless of a ball, a semi-sphere, a pellet, a ring, and amorphism, the alumina usually used as desirable support for silver catalysts, silica alumina, a zirconia, a magnesia, silicon carbide, etc. are desirable, and stainless steel, alpha-alumina, and a zirconia are [that what is necessary is just an inactive refractoriness object] especially desirable. The configuration of such inactive refractoriness support, a dimension, a hole, specific surface area, apparent porosity, etc. can be suitably chosen in consideration of the pressure loss at the time of filling up a coil, and a mechanical strength. 16 - 1/2 inch per /, mean diameters are 3 / 16 - 1/2 inch, and a ball thru/or its ring-like object are usually preferably desirable. Moreover, what deposited at least one sort chosen as the above-mentioned inactive refractoriness support from sodium, a potassium, a rubidium, caesium, a lithium, calcium, strontium, barium, and a thallium can use it suitably, and sodium, a potassium, a rubidium, caesium, and a thallium are especially desirable. As for especially these, it is desirable to fill up the coil of the inactive substance restoration section.

[0021] The process and reaction condition which can apply this invention approach can apply both a well-known process and a reaction condition in this field conventionally. For example, the process which carries out contact vapor phase oxidation of the ethylene by molecular oxygen, and manufactures ethylene oxide can apply this invention approach effectively [in any case], although there are an air-oxidation method for using air as a source of oxygen and an oxygen acid-ized method using pure

oxygen. The oxygen acid-ized method which can enlarge reacting weight per one catalyst bed passage, and can make ethylene oxide concentration high especially can apply effectively.

[0022] Although material gas mixture consists of reaction inhibitors, such as ethylene, oxygen, carbon dioxide gas, nitrogen, an argon, methane, ethane, and 2 chlorination ethane, etc. in the operating condition, and ethylene concentration is so advantageous that it is high, it is 15 to 35 capacity % especially below 40 capacity %. Especially carbon dioxide gas is four to 8 capacity % below 10 capacity %. Moreover, since methane has the operation which shifts range of explosion to an insurance side, and narrows range of explosion when methane or ethane is made to exist in gas, it is effective to exist by high concentration considerably as a reactant gas diluent.

[0023] Reaction pressure is 1.08-3.04MPa preferably 0.59 to 4.02 MPa. 150-300 degrees C of reaction temperature are 180-280 degrees C preferably. space velocity -- 1000-10000hr-1 -- it is 2000-8000hr-1 preferably.

[0024] Although all of a well-known silver catalyst can be conventionally used for the catalyst with which the reaction section is filled up Preferably below specific surface area of $20\text{m}^2/\text{g}$ to $10\text{m}^2/\text{g}$. What carried out deposit support of the metal silver of a minute amount is preferably good for the inactive refractoriness support of 30 - 70 capacity % more than apparent porosity 20 capacity %. Moreover, what added at least one sort chosen from at least a kind of alkali metal and the alkaline earth metal which are chosen from caesium, a potassium, and a rubidium as a reaction accelerator, a thallium, antimony, tin, etc. is desirable. The inactive refractoriness support which can use inactive refractoriness support, such as an alumina, a silica alumina, silicon carbide, a zirconia, and a magnesia, as a support ingredient, and uses especially alpha-alumina as a principal component is desirable. Although the configuration of support has a ball, a semi-sphere, a ring, a pellet, etc., a ball thru/or its ring are desirable. Moreover, the mean diameter has desirable $1/16$ - $1/2$ inch, and especially its $3/16$ - $5/16$ inch are desirable. The amount of the silver supported is good at 1 - 20 % of the weight in a catalyst, and 5 - 15% of the weight of its range is substantially economical especially.

[0025] In order to explain this invention in more detail, a drawing explains. A drawing does not show 1 of the embodiment at the time of carrying out contact vapor phase oxidation of the ethylene by molecular oxygen content gas, and the equipment used under existence of a silver catalyst, and does not restrain this invention.

[0026] In drawing 1, it consists of many coils. To the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 which formed the preheating section 4 which filled up the inlet-port section of a coil with the inactive substance, and with which it was filled up, the reaction section 5 filled up with the silver catalyst between the inlet-port section of a coil, and the outlet section, or the inert-packing-material restoration section 6 which filled up the outlet section of a coil with the inert packing material, and ethylene, oxygen, The temperature containing reaction inhibitors, such as carbon dioxide gas, nitrogen and an argon, methane, ethane, and 2 chlorination ethane, etc. of 100-200 degrees C, It is introduced from a conduit 1. desirable -- 150-190-degree C material gas -- material gas supply -- pass the preheating section 4, the reaction section 5, and the inert-packing-material restoration section 6 -- reaction generation gas -- 200-300 degrees C is preferably sent to the condensator 11 for cooling of 210-280-degree C reaction generation gas through a conduit 7.

[0027] This invention consists of many coils 3. And between the preheating section 4 and the inlet-port section of a coil which filled up the inlet-port section of a coil with the inactive substance and with which it was filled up, and the outlet section A silver catalyst In the reaction section 5 with which it was filled up, or the outlet section of a coil, an inert packing material The inert-packing-material restoration section 6 with which it was filled up The established silver catalyst of the vertical mold multipipe heat exchange mold reactor 2 At the place left without adjoining the reaction section 5 with which it was filled up reaction generation gas It is effective in the process which installed the condensator for cooling reaction generation gas in the place left without adjoining the inert-packing-material restoration section 6 filled up with the process which installed the condensator 11 for cooling, or the silver catalyst of the vertical mold multipipe heat exchange mold reactor 2. A condensator 11 has a condensator with a heat exchanger, water, air, etc. for carrying out heat exchange of the material gas and reaction generation gas

which are supplied to the boiler for heat recovery, and a reactor etc.

[0028] Supply of the inert gas of this invention can supply inert gas to the stagnation section of reaction generation gas, such as an expansion joint for the destructive prevention by the thermal stress of the manhole of the working-level month installed in the 200-300-degree C reaction generation gas stream band between the down-stream heat exchangers 11 from the coil outlet of the vertical mold multipipe heat exchange mold reactor 2, a relief valve, a rupture disk, a manometer, a thermometer, and the piping section. drawing 1 -- setting -- the gas stagnation section 9 of an expansion joint 8 -- inert gas supply -- inert gas is supplied from a conduit.

[0029] The gas stagnation section which exists in the reaction generation gas stream band of 200-300 degrees C of lower streams of rivers from the coil outlet of the reactor of this invention can be filled up with the inactive substance of a network, Paul ring, Raschig ring, and a saddle configuration.

[0030] drawing 2 shows other embodiments of this invention, and the gas stagnation section 12 forms it in the manhole 14 of the lower part of a reactor 2 -- having -- inert gas supply -- inert gas is supplied to the gas stagnation section from a conduit 13. In addition, in this drawing, the same sign as drawing 1 expresses the same member.

[Translation done.]

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OPERATION

[Function] the lower part [section / of the reactor at the time of carry out contact vapor phase oxidation of this invention by said ethylene and molecular oxygen which be carried out , and manufacture ethylene oxide / coil outlet] -- and while cancel generating of an abnormalities combustion reaction in the gas stagnation section which exist in exist in the reaction generation gas stream band of a before [a heat exchanger] , the stability of thermal efficiency aim at and the operation which can increase the effectiveness which control the isomerization to the acetaldehyde which be an impurity offer .

[Translation done.]

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EXAMPLE

[Example] Hereafter, an example explains this invention in more detail. However, this example is one mode of invention and does not regulate this invention.

[0033] In example 1 drawing 1 Ethylene 20 capacity %, Through a conduit 1, space-velocity 5000hr-1 appears in the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 comparatively, and it introduces. the material gas of 2.36MPa(s) by which the preheating was carried out to the temperature containing molecular oxygen 8 capacity % and carbon-dioxide 6 capacity % of 180 degrees C -- material gas supply -- pass the preheating section 4 filled up with the inactive substance, the reaction section 5 filled up with the silver catalyst, and the inactive substance restoration section 6 -- the 242-degree C reaction generation gas containing generation ethylene oxide 2 capacity % -- reaction generation gas -- it sent to the condensator 11 through the conduit 7.

[0034] on the other hand -- the reaction generation gas of the coil outlet of the multipipe heat exchange mold reactor 2 -- a conduit 7 and reaction generation gas -- the gas stagnation section 9 (phi650mmx660mm and 0.22m3) (temperature of 242 degrees C) of the expansion-joint section 8 for piping thermal stress prevention installed between conduits 10 -- inert gas supply -- nitrogen gas was supplied through the conduit 10. the reaction generation gas of the downstream of after 1000-hour operation and the expansion joint 8 for piping thermal stress prevention -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 0.05 capacity ppm and the aldehyde 2 capacity ppm. Moreover, as a result of carrying out the release check of the gas stagnation section 7, there was no adhesion generation of carbide. A result is shown in Table 1.

[0035] example of comparison 1 example 1 -- setting -- the gas stagnation section 9 of the expansion-joint section 8 for piping thermal stress prevention -- inert gas supply -- it carried out like the example 1 except not supplying nitrogen gas through a conduit 10. After 13-hour operation, since the temperature of suddenly reaction generation gas rose to 316 degrees C, urgent shutdown was carried out. the reaction generation gas of the downstream of the expansion joint 8 for piping thermal stress prevention -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 5000 capacity ppm and the aldehyde 1000 capacity ppm (as an acetaldehyde). Moreover, as a result of carrying out the release check of the gas stagnation section 9, adhesion generation of carbide was seen. A result is shown in Table 1.

[0036]

[Table 1]

| | | 実施例 1 | 比較例 1 |
|---------------------------|-------|--------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.22 | 0.22 |
| ガス滞留時間 (min) | 滞留部 9 | 404 | 780 |
| 窒素ガス投入量 (NI/min) | 導管 10 | 7 | 0 |
| 反応生成ガス温度 (°C) | 導管 7 | 242 | 242→316 |
| CO濃度 (ppm) | 導管 7 | 0.05以下 | 1→ 5000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→ 1000 |

[0037] In example 2 drawing 2 Ethylene 20 capacity %, Through a conduit 1, space-velocity 5000hr-1 appears in the coil 3 of the vertical mold multipipe heat exchange mold reactor 2 comparatively, and it introduces. the material gas of 2.36MPa(s) by which the preheating was carried out to the temperature containing molecular oxygen 8 capacity % and carbon-dioxide 6 capacity % of 180 degrees C -- material gas supply -- pass the preheating section 4 filled up with the inactive substance, and the reaction section 5 filled up with the silver catalyst -- the 244-degree C reaction generation gas containing generation ethylene oxide 2 capacity % -- reaction generation gas -- it sent to the condensator (not shown) through the conduit 7.

[0038] on the other hand -- the coil outlet of the multipipe heat exchange mold reactor 2, and reaction generation gas -- the gas stagnation section 12 (phi600mmx600mm and 0.17m³) of the manhole 14 installed between conduits 7 -- inert gas supply -- carbon dioxide gas was supplied through the conduit 13. the reaction generation gas of the downstream of after 1200-hour operation and a manhole 8 -- as a result of a conduit's 7 analyzing, it was the aldehyde 2 capacity ppm below the carbon monoxide 0.05 capacity ppm. Moreover, as a result of carrying out the release check of the gas stagnation section 12, there was no adhesion generation of carbide. A result is shown in Table 2.

[0039] example of comparison 2 example 2 -- setting -- the gas stagnation section 12 of a manhole 14 -- inert gas supply -- it carried out like the example 2 except not supplying carbon dioxide gas through a conduit 13. After 20-hour operation, since the temperature of suddenly reaction generation gas rose to 314 degrees C, urgent shutdown was carried out. the reaction generation gas of the downstream of the gas stagnation section 12 of a manhole 14 -- as a result of a conduit's 7 analyzing, they were the carbon monoxide 6000 capacity ppm and the aldehyde 1300 capacity ppm (as an acetaldehyde). Moreover, as a result of carrying out the release check of the gas stagnation section 9, adhesion generation of carbide was seen. A result is shown in Table 2.

[0040]

[Table 2]

| | | 実施例 2 | 比較例 2 |
|---------------------------|-------|--------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.17 | 0.17 |
| ガス滞留時間 (min) | 滞留部 9 | 437 | 1200 |
| 炭酸ガス投入量 (NI/min) | 導管 10 | 5 | 0 |
| 反応生成ガス温度 (℃) | 導管 7 | 244 | 244→314 |
| CO濃度 (ppm) | 導管 7 | 0.05以下 | 1→ 6000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→ 1300 |

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view having shown one embodiment of the ethylene oxide manufacture approach by ** and this invention.

[Drawing 2] It is the explanatory view having shown other embodiments of the ethylene oxide manufacture approach by ** and this invention.

[Description of Notations]

- 1: material gas supply -- a conduit,
- 2: Vertical mold multipipe heat exchange mold reactor,
- 3: Coil,
- 4: Preheating section,
- 5: Reaction section,
- 6: Inactive substance restoration section,
- 7: reaction generation gas -- a conduit,
- 8: The expansion joint for piping thermal stress prevention,
- 9 12: Gas stagnation section,
- 10 and 13:inert gas supply -- a conduit,
- 11: Condensator,
- 14: Manhole.

[Translation done.]

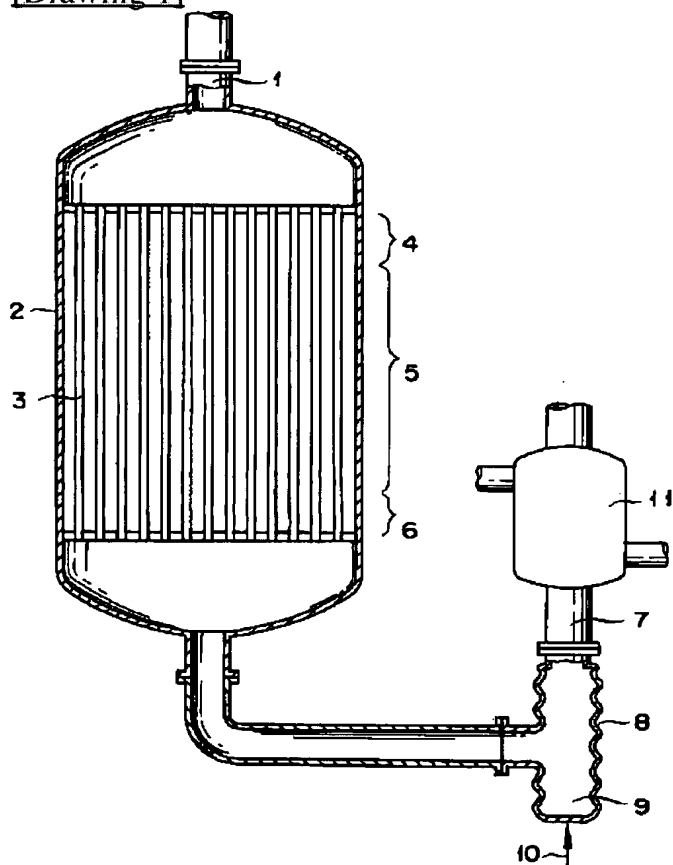
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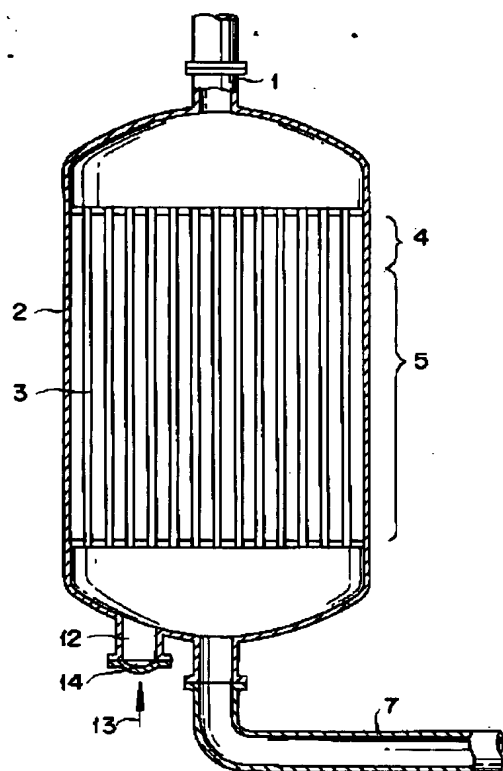
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

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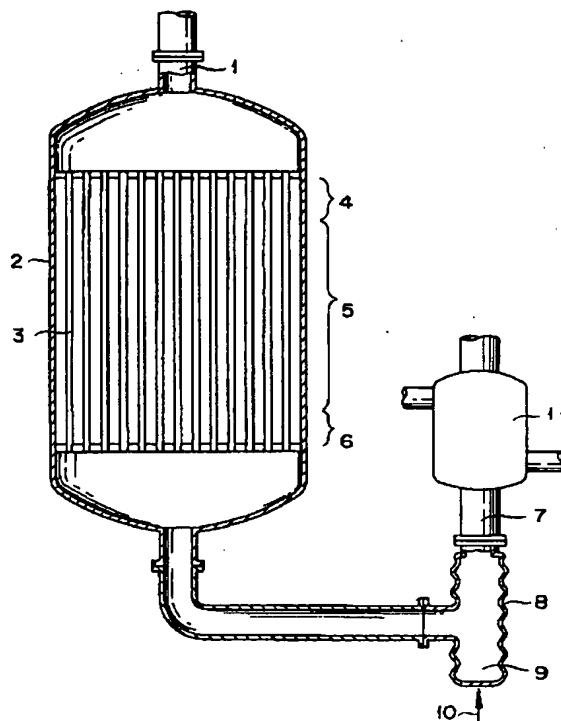
(54)【発明の名称】 エチレンオキシドの製造方法

(57)【要約】

【目的】 本発明は、エチレンと分子状酸素により接触気相酸化してエチレンオキシドを製造する際の反応器の反応管出口より下流に存在する高温部のガス滞留部において異常燃焼反応を防ぐエチレンオキシドの製造方法を提供することを目的とする。

【構成】 エチレンを分子状酸素含有ガスにより接触気相酸化してエチレンオキシドを製造する際に使用する反応器の反応管出口より下流でかつ冷却器までの間の反応生成ガス流帯域に存在するガス滞留部に不活性ガスを供給することを特徴とするエチレンオキシドの製造方法。

【効果】 エチレンを分子状酸素により接触気相酸化してエチレンオキシドを製造するにあたって安全な方法である。



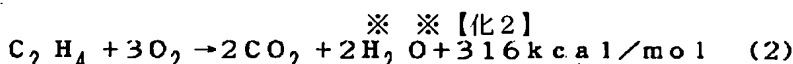
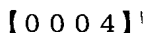
* 関するものである。

【0002】

【従来の技術】エチレンの接触気相酸化反応、例えばエチレンを銀触媒の存在下に分子状酸素により接触気相酸化してエチレンオキシドを製造するプロセスにおいては、エチレンの他にメタン、エタン等の飽和炭化水素、窒素、二酸化炭素、アルゴン、酸素等を含有する炭化水素含有ガスと空気、酸素を富化した空気または純酸素からなる分子状酸素含有ガスとが所定の比率で混合されたのち、銀触媒を充填した反応器に導入された接触気相反応が行なわれる。その際エチレンを銀触媒の存在下に分子状酸素により反応させると、

【0003】

【化1】

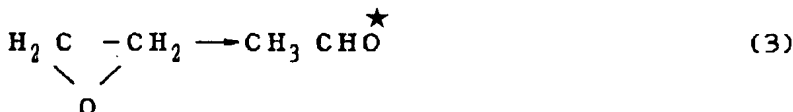


20★【0007】また、前記反応式(1)および反応式

(2) 以外に、エチレンオキシドの収率に影響を及ぼす反応がある。それは生成したエチレンオキシドのつぎの反応式(3)で示す反応式で進行するアセトアルデヒドへの異性化反応である。

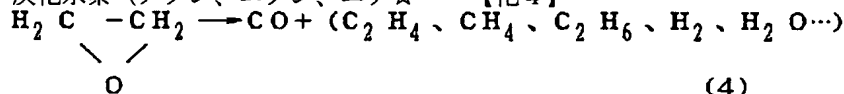
【0008】

【化3】



☆レン等)、水素および水への異常反応がある。反応器の反応管出口より下流の反応生成ガス流帯域は高温であるために、異常反応をなくすることが、エチレンオキシド製造における大きな課題の一つである。

【0011】



40 た、このような方法を、エチレンの分子状酸素による接触相酸化法によりエチレンオキシドを製造する方法に適用することも公知である。たとえば特開昭51-4101号によれば、反応域に隣接したあるいは隣接しないでかつ不活性材料を含有したあるいは含有しない冷却域に反応域で得られる反応生成物を通過させている。また、特開昭53-2409号によれば、反応生成物を $0.1 \text{ m}^2 / \text{g}$ 以下の表面積を有する不活性耐火粒状物を充填した冷却域に通過させている。

【0014】

【発明が解決しようとする課題】 従来、エチレンと分子

状酸素により接触気相酸化してエチレンオキシドを製造する際の使用されている反応器の多管式熱交換型反応器は、安全性、作業性用のマンホール（特開昭 54-32408 号記載の図面、特開昭 63-190881 号記載の図面）、異常圧力上昇防止の安全弁および破裂板、圧力計、温度計、配管部の熱応力による破壊防止のためのエクспанションジョイントなどがあり、ガス滞留部が存在する。しかるに、これらのガス滞留部で異常燃焼反応が起るとい問題があった。

【0015】本発明は、前記したエチレンと分子状酸素により接触気相酸化してエチレンオキシドを製造する際の反応器の反応管出口より下流の 200～300℃の反応生成ガス流帯域に存在するガス滞留部において異常燃焼反応を防ぐエチレンオキシドの製造方法を提供することにある。

【0016】

【課題を解決するための手段】本発明は、エチレンを分子状酸素含有ガスにより接触気相酸化してエチレンオキシドを製造する際に使用する反応器の反応管出口より下流でかつ冷却器の間の反応生成ガス流帯域に存在するガ

ガス滞留時間 (min)

＝滞留部容積 (m³) / 実際の温度圧力下での不活性ガス流量 (m³ / min)

【0020】本発明の反応器の予熱部と不活性物質充填部に充填する不活性充填物としては、不活性耐火性物であればよく、球、半球、ペレット、リングおよび無定形を問わずいずれも使用できるが、好ましくは銀触媒用の担体として通常使用されるアルミナ、シリカーアルミナ、ジルコニア、マグネシア、炭化ケイ素等が好ましく、特にステンレス、 α -アルミナおよびジルコニアが好ましい。これらの不活性耐火性担体の形状、寸法、孔、比表面積、見かけの気孔率等は反応管に充填した際の圧力損失、機械的強度を考慮して適当に選ぶことができる。平均粒径は通常 1/16～1/2 インチ、好ましくは 3/16～1/2 インチであり、球ないしリング状物が好ましい。また、上記不活性耐火性担体にナトリウム、カリウム、ルビジウム、セシウム、リチウム、カルシウム、ストロンチウム、バリウムおよびタリウムから選ばれた少なくとも 1 種を析出させたものが好適に使用でき、特にナトリウム、カリウム、ルビジウム、セシウムおよびタリウムが好ましい。これらは特に、不活性物質充填部の反応管に充填することが好ましい。

【0021】本発明方法を適用し得るプロセスおよび反応条件は、従来この分野で公知のプロセスおよび反応条件のいずれも適用できる。たとえば、エチレンを分子状酸素で接触気相酸化してエチレンオキシドを製造するプロセスは、酸素源として空気を用いる空気酸化法と純酸素を用いる酸素酸化法とがあるが、本発明方法はいずれの場合にも有効に適用できる。特に触媒層 1 回通過当りの反応量を大きくすることができ、エチレンオキシド濃度を高くすることができる酸素酸化法が有効に適用でき

* ス滞留部に不活性ガスを供給することを特徴とするエチレンオキシドの製造方法に関するものである。

【0017】本発明において反応器のガス出口部のガス滞留部は、エチレンと分子状酸素により接触気相酸化してエチレンオキシドを製造する際の使用されている反応器、例えば多管式熱交換型反応器の反応管出口に設置される通路用のマンホール、安全弁、破裂板、圧力計、温度計および配管部の熱応力による破壊防止のためのエクспанションジョイントなどがある。このようなガス滞留部の温度は、200～300℃、好ましくは 210～280℃である。

【0018】本発明で使用する不活性ガスとしてはたとえば窒素、炭酸ガス、メタン、アルゴンなど挙げられ、好ましくは窒素である。不活性ガスの供給量は、前記反応生成ガスの滞留部に下記の式で定義するガス滞留時間が 12 時間以内、好ましくは 1～1.0 時間、さらに好ましくは 3～8 時間となるように供給することができる。

【0019】

【数 1】

る。

【0022】操作条件は、原料ガス混合物はエチレン、酸素、炭酸ガス、窒素、アルゴン、メタン、エタンおよび二塩化エタン等の反応抑制剤等からなっており、エチレン濃度は高いほど有利であるが、40 容量%以下、特に 15～35 容量%である。炭酸ガスは 10 容量%以下、特に 4～8 容量%である。また、メタンまたはエタンをガス中に存在させた場合、メタンは爆発範囲を安全側にずらし、爆発範囲を狭くする作用があるので、反応ガス希釈剤としてかなり高濃度で存在することが有効である。

【0023】反応圧力は 0.59～4.02 MPa、好ましくは 1.08～3.04 MPa である。反応温度は 150～300℃、好ましくは 180～280℃である。空間速度は 1000～10000 hr⁻¹、好ましくは 2000～8000 hr⁻¹ である。

【0024】反応部に充填される触媒は、従来公知の銀触媒のいずれも使用できるが、比表面積 20 m² / g 以下、好ましくは 0.01～10 m² / g、見かけの気孔率 20 容量%以上、好ましくは 30～70 容量%の不活性耐火性担体に微量の金属銀を析出担持したものがよく、また反応促進剤としてセシウム、カリウムおよびルビジウムから選ばれる少なくとも一種のアルカリ金属、アルカリ土類金属、タリウム、アンチモン、スズ等から選ばれる少なくとも 1 種を添加したものが好ましい。担体材料としてアルミナ、シリカーアルミナ、シリコンカーバイド、ジルコニア、マグネシア等の不活性耐火性担体を使用でき、特に α -アルミナを主成分とする不活性

耐火性担体が好ましい。担体の形状は球、半球、リング、ペレット等があるが球ないし、リングが好ましい。また、その平均粒径は1/16~1/2インチが好ましく、特に3/16~5/16インチが好ましい。担持される銀の量は触媒中に1~20重量%でよく、特に5~15重量%の範囲が実質的に経済的である。

【0025】本発明をさらに詳しく説明するために、図面により説明する。図面は銀触媒の存在下、エチレンを分子状酸素含有ガスにより接触気相酸化する際の実施態様および使用される装置の一を示すもので、本発明を拘束するものではない。

【0026】図1において、多数の反応管で構成され、かつ反応管の入口部に不活性物質を充填した充填した予熱部4、反応管の入口部と出口部の間に銀触媒を充填した反応部5、または反応管の出口部に不活性充填物を充填した不活性充填物充填部6を設けた縦型多管式熱交換型反応器2の反応管3に、エチレン、酸素、炭酸ガス、窒素およびアルゴン、メタン、エタン、二塩化エタン等の反応抑制剤等を含む温度100~200℃、好ましくは150~190℃の原料ガスは原料ガス供給導管1より導入され、予熱部4、反応部5および不活性充填物充填部6を経て、反応生成ガス導管7を通して200~300℃、好ましくは210~280℃の反応生成ガスが冷却のための冷却器11に送られる。

【0027】本発明は多数の反応管3で構成され、かつ反応管の入口部に不活性物質を充填した充填した予熱部4、反応管の入口部と出口部の間に銀触媒を充填した反応部5、または反応管の出口部に不活性充填物を充填した不活性充填物充填部6を設けた縦型多管式熱交換型反応器2の銀触媒を充填した反応部5に隣接せずに離れたところに反応生成ガスを冷却するための冷却器11を設置したプロセスまたは縦型多管式熱交換型反応器2の銀触媒を充填した不活性充填物充填部6に隣接せずに離れたところに反応生成ガスを冷却するための冷却器を設置したプロセスに有効である。冷却器11は、熱回収のためのボイラー、反応器に供給する原料ガスと反応生成ガスとを熱交換するための熱交換器、水および空気等による冷却器等がある。

【0028】本発明の不活性ガスの供給は、縦型多管式熱交換型反応器2の反応管出口より下流の熱交換器11の間の200~300℃の反応生成ガス流帯域に設置される作業用のマンホール、安全弁、破裂板、圧力計、温度計および配管部の熱応力による破壊防止のためのエキスパンションジョイントなどの反応生成ガスの滞留部に不活性ガスを供給することができる。図1においては、エキスパンションジョイント8のガス滞留部9に不活性ガス供給導管より不活性ガスを供給するものである。

【0029】本発明の反応器の反応管出口より下流200~300℃の反応生成ガス流帯域に存在するガス滞留部には網、ポールリング、ラシヒリング、サドル形状の

不活性物質を充填することができる。

【0030】図2は、本発明の他の実施態様を示すもので、反応器2の下部のマンホール14にガス滞留部12が形成され、不活性ガス供給導管13より不活性ガスがガス滞留部に供給される。なお、同図において、図1と同一の符号は同一部材を表わす。

【0031】

【作用】本発明は、前記したエチレンと分子状酸素により接触気相酸化してエチレンオキシドを製造する際の反応器の反応管出口部より下部でかつ熱交換器までの間の反応生成ガス流帯域に存在するガス滞留部において異常燃焼反応の発生を解消するとともに、熱効率の安定を図り、不純物であるアセトアルデヒドへの異性化反応を抑制する効果を増大させることができる作用を提供するものである。

【0032】

【実施例】以下、実施例により、この発明をさらに詳しく説明する。しかし、この実施例は発明の一態様であって、この発明を規制するものではない。

【0033】実施例1

図1において、エチレン20容量%、分子状酸素8容量%および二酸化炭素6容量%を含む温度180℃に予熱された2.36MPaの原料ガスは原料ガス供給導管1を通して縦型多管式熱交換型反応器2の反応管3に空間速度5000hr⁻¹の割合で導入し、不活性物質を充填した予熱部4、銀触媒を充填した反応部5および不活性物質充填部6を経て、生成エチレンオキシド2容量%を含む242℃の反応生成ガスを反応生成ガス導管7を通して冷却器11に送った。

【0034】一方、多管式熱交換型反応器2の反応管出口の反応生成ガス導管7と反応生成ガス導管10の間に設置される配管熱応力防止用エキスパンションジョイント部8のガス滞留部9(φ650mm×660mm、0.22m³) (温度242℃)に不活性ガス供給導管10を通して窒素ガスを供給した。1000時間運転後、配管熱応力防止用エキスパンションジョイント8の下流側の反応生成ガス導管7で分析をした結果、一酸化炭素0.05容量ppm、アルデヒド2容量ppmであった。またガス滞留部7を解放点検した結果、炭化物の付着生成はなかった。結果は表1に示す。

【0035】比較例1

実施例1において、配管熱応力防止用エキスパンションジョイント部8のガス滞留部9に不活性ガス供給導管10を通して窒素ガスを供給しない以外は実施例1と同様に行なった。13時間運転後、突然反応生成ガスの温度が316℃まで上昇したため緊急運転停止した。配管熱応力防止用エキスパンションジョイント8の下流側の反応生成ガス導管7で分析した結果、一酸化炭素5000容量ppm、アルデヒド(アセトアルデヒドとして)1000容量ppmであった。またガス滞留部9を解放点

検した結果、炭化物の付着生成が見られた。結果は表 1 に示す。

* 【0036】

* 【表 1】

| | | 実施例 1 | 比較例 1 |
|---------------------------|-------|---------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.22 | 0.22 |
| ガス滞留時間 (min) | 滞留部 9 | 404 | 780 |
| 窒素ガス投入量 (NI/min) | 導管 10 | 7 | 0 |
| 反応生成ガス温度 (°C) | 導管 7 | 242 | 242→316 |
| CO 濃度 (ppm) | 導管 7 | 0.05 以下 | 1→ 5000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→ 1000 |

【0037】実施例 2

図 2 において、エチレン 20 容量%、分子状酸素 8 容量%および二酸化炭素 6 容量%を含む温度 180°C に予熱された 2.36 MPa の原料ガスは原料ガス供給導管 1 を通して縦型多管式熱交換型反応器 2 の反応管 3 に空間速度 5000 hr⁻¹ の割合で導入し、不活性物質を充填した予熱部 4、銀触媒を充填した反応部 5 を経て、生成エチレンオキシド 2 容量%を含む 244°C の反応生成ガスを反応生成ガス導管 7 を通して冷却器 (図示してない) に送った。

【0038】一方、多管式熱交換型反応器 2 の反応管出口と反応生成ガス導管 7 の間に設置されるマンホール 14 のガス滞留部 12 (φ 600 mm×600 mm、0.17 m³) に不活性ガス供給導管 13 を通して炭酸ガスを供給した。1200 時間運転後、マンホール 8 の下流側の反応生成ガス導管 7 で分析をした結果、一酸化炭素※

※ 0.05 容量 ppm 以下、アルデヒド 2 容量 ppm であった。またガス滞留部 12 を解放点検した結果、炭化物の付着生成はなかった。結果は表 2 に示す。

【0039】比較例 2

実施例 2 において、マンホール 14 のガス滞留部 12 に不活性ガス供給導管 13 を通して炭酸ガスを供給しない以外は実施例 2 と同様に行なった。20 時間運転後、突然反応生成ガスの温度が 314°C まで上昇したため緊急運転停止した。マンホール 14 のガス滞留部 12 の下流側の反応生成ガス導管 7 で分析した結果、一酸化炭素 6000 容量 ppm、アルデヒド (アセトアルデヒドとして) 1300 容量 ppm であった。またガス滞留部 9 を解放点検した結果、炭化物の付着生成が見られた。結果は表 2 に示す。

【0040】

【表 2】

| | | 実施例 2 | 比較例 2 |
|---------------------------|-------|---------|---------|
| ガス滞留部容積 (m ³) | 滞留部 9 | 0.17 | 0.17 |
| ガス滞留時間 (min) | 滞留部 9 | 437 | 1200 |
| 炭酸ガス投入量 (NI/min) | 導管 10 | 5 | 0 |
| 反応生成ガス温度 (°C) | 導管 7 | 244 | 244→314 |
| CO 濃度 (ppm) | 導管 7 | 0.05 以下 | 1→ 6000 |
| アルデヒド濃度 (ppm) | 導管 7 | 2 | 5→ 1300 |

【0041】

【発明の効果】本発明は前記したエチレンと分子状酸素により接触相酸化してエチレンオキシドを製造する際の反応器の反応管出口部に存在する 200~300°C の

高温部より下流でかつ冷却器までの間の反応生成ガス流帯域に存在するガス滞留部において異常燃焼反応の発生を解消するとともに、熱効率の安定を図り、不純物であるアセトアルデヒドへの異性化反応を抑制する効果を増

大させることができる効果を有する。

【図面の簡単な説明】

【図 1】は、本発明によるエチレンオキシド製造方法の一実施態様を示した説明図である。

【図 2】は、本発明によるエチレンオキシド製造方法の他の実施態様を示した説明図である。

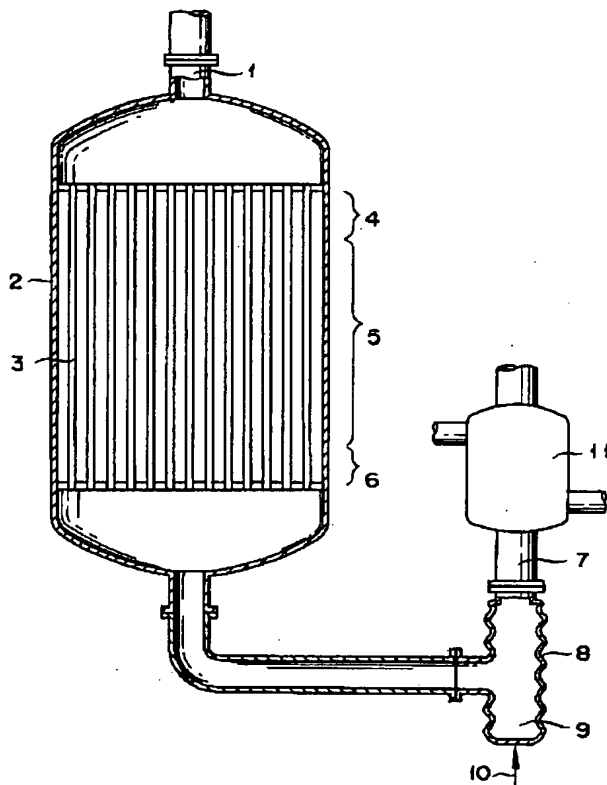
【符号の説明】

- 1：原料ガス供給導管、
2：縦型多管式熱交換型反応器、
3：反応管、

- * 4：予熱部、
5：反応部、
6：不活性物質充填部、
7：反応生成ガス導管、
8：配管熱応力防止用エクステンションジョイント、
9、12：ガス滞留部、
10、13：不活性ガス供給導管、
11：冷却器、
14：マンホール。

*10

【図 1】



【図 2】

